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### NONIONIC HYDROGELS BASED ON POLY(METHYL TRIETHYLENE GLYCOL VINYL ETHER)

Lunhan Ding<sup>a</sup>; Sergey E. Evsyukov<sup>b</sup>

<sup>a</sup> Department of Chemistry, 1393 H. C. Brown Laboratory of Chemistry, Purdue University, West Lafayette, IN, U.S.A. <sup>b</sup> Polymer Laboratory, Ludwigshafen, Germany

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## NONIONIC HYDROGELS BASED ON POLY(METHYL TRIETHYLENE GLYCOL VINYL ETHER)

Lunhan Ding<sup>†</sup> and Sergey E. Evsyukov<sup>\*</sup>

Polymer Laboratory, BASF Aktiengesellschaft, ZKS/A – B 1,  
67056 Ludwigshafen, Germany

### ABSTRACT

Two types of nonionic hydrogels have been synthesized in the present study by cationic polymerization. The first type was prepared by precipitative copolymerization of methyl triethylene glycol vinyl ether (MTVE) and tetraethylene glycol divinyl ether (TDVE). Methyl tert-butyl ether (MTBE) was used as a polymerization medium, because it is a good solvent for the monomers but not a solvent for their copolymer. The swelling capacity of the copolymers was found to reach its maximum (10 g/g), when the content of TDVE used as a crosslinker was 5 wt%.

Another type was synthesized by cationic copolymerization of MTVE and vinyloxyethyl methacrylate (VEM) followed by the radical crosslinking. The monomers were first copolymerized in dichloromethane at  $-78^{\circ}\text{C}$  to afford a water-soluble copolymer in almost quantitative yield. Then the copolymers were crosslinked using ammonium persulfate as a radical initiator. The crosslinked products containing 0.3 wt% of VEM exhibited maximum swellability in water (24 g/g).

Both types of hydrogels were shown to be stable in the presence of an electrolyte salt as well as over a wide pH range of aqueous media.

*Key Words:* Vinyl ethers; Methyl triethylene glycol vinyl ether; Vinyloxyethyl methacrylate; Cationic polymerization; Radical crosslinking; Hydrogels

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\*Corresponding author.

<sup>†</sup>Present address: Department of Chemistry, Purdue University, 1393 H. C. Brown Laboratory of Chemistry, West Lafayette, IN 47907-1393.

## INTRODUCTION

Hydrogels are loosely crosslinked polymer networks characterized by their hydrophilicity and insolubility in water. The softness, elasticity, and capability of absorbing and storing large amounts of liquids make hydrogels unique materials. Based on hydrogels, many researchers are developing artificial muscles for robots and tissues for human prosthetics, controlled drug delivery systems, chemical valves that control the flow of liquids, sensors, actuators, matrices for molecular recognition or separation (1–4). Moreover, hydrogels are widely used as superabsorbent materials in hygienic personal care products (e.g., diapers), soil improvers for agriculture and horticulture, and thickeners in cosmetics and paints (5–8). In some application areas the hydrogels are supposed to keep their swelling ability under conditions of different and/or variable pH values of aqueous media as well as in the presence of various electrolytes in them. Consequently, there was and still is a substantial interest among scientists in the field of nonionic hydrogels, e.g., those based on poly(*N*-vinylpyrrolidone) (9), poly(acrylamide) (10), poly(hydroxyethyl methacrylate) (11), and, particularly, poly(ethyleneglycol) (12) and its derivatives inasmuch as these gels contain no ionic groups in their structures and generally are insensitive to alterations of pH or to the presence of electrolytes.

Methyl triethylene glycol vinyl ether (MTVE) was reported to readily polymerize by cationic initiators, yielding a highly viscous liquid polymer, poly(methyl triethylene glycol vinyl ether) (PMTVE), which is soluble in water and common organic solvents (13–15). The present article reports on the synthesis of PMTVE hydrogels with the use of tetraethylene glycol divinyl ether (TDVE) as a crosslinking agent or vinyloxyethyl methacrylate (VEM) as a crosslinkable comonomer. The swelling behavior of the hydrogels in the presence of NaCl at different concentrations and over a broad pH range has also been studied.

## EXPERIMENTAL

### Materials

MTVE and TDVE were dried with calcium hydride for 2 days and distilled under reduced pressure. Methyl tert-butyl ether and dichloromethane were dried with CaH<sub>2</sub> for 3 days and distilled before use. VEM was prepared according to a reported procedure (16,17) and distilled over calcium hydride before use. BF<sub>3</sub>·Et<sub>2</sub>O was purchased from Fluka. Ammonium persulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TMED) were purchased from Aldrich.

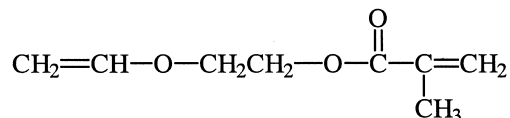
### Cationic Precipitative Polymerization of MTVE

The distillation and polymerization glassware was dried using a heatgun and flushed with nitrogen. In a typical polymerization procedure, 20 mL of methyl butyl ether, 4 mL of MTVE, and 0.2 mL of TDVE were introduced through a rub-



MTVE

TDVE



VEM

*Structure 1.*

ber septum into a conical flask using a syringe and cooled down to  $-78^\circ\text{C}$  with the use of an acetone/dry ice bath. Then, 0.3 mL of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  were added to the reaction mixture while stirring with a magnet bar. In a couple of minutes the stirring was stopped, and a crosslinked copolymer started to gradually precipitate from the solution. After 1 h, the polymerization was terminated with methanol and further quenched with an equivalent amount of a methanolic ammonia solution. Finally, the reaction product was washed with a plenty of water to remove the rest of initiator and dried at  $70^\circ\text{C}$  under reduced pressure to afford crosslinked PMTVE as colorless pieces in 85% yield.

### Cationic Copolymerization of MTVE with VEM Followed by Radical Crosslinking

Typically, 40 mL of dichloromethane (DCM), 15 mL of MTVE, and 0.06 mL of VEM were injected into a dried (as above) reaction flask via a syringe. The flask was then cooled down to  $-78^\circ\text{C}$ , using an acetone/dry ice bath, and 0.2 mL of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  were added to the reaction mixture. After the reaction was allowed to proceed at  $-78^\circ\text{C}$  for 1 h, it was quenched with an equivalent amount of a methanolic ammonia solution. The solvents were evaporated at  $50^\circ\text{C}$  under reduced pressure to afford a colorless polymer that was readily soluble in water. For analytical purposes the reaction mixture was diluted by adding 40 mL of DCM and extracted with distilled water ( $4 \times 50$  mL). Finally, the solvent was removed under reduced pressure to leave the product as a highly viscous colorless liquid. Its proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded on a Bruker DOX 200 spectrometer, using acetone- $d_6$  as a solvent. The  $^1\text{H}$  NMR spectra of the MTVE-VEM copolymers exhibit a weak peak at 5.6 ppm attributable to protons at the  $\beta$ -carbon atom in the methacrylate groups. The content of these groups calculated on the basis of spectroscopic data was normally found to be consistent with the composition of monomer mixtures used to prepare the samples. Gel permeation chromatography (GPC) measurements were carried out in tetrahydrofuran (THF) at  $25^\circ\text{C}$ .

To synthesize hydrogels, to 25 g of a 20% aqueous solution of the copolymer were added 5% aqueous solutions of APS and TMED (0.3 mL each), the mixture

was agitated and allowed to stay at room temperature for 24 h to produce a gel. The gel was then extracted with a plenty of frequently changed water for 4 days to remove salts. Finally, the gel was dried at 70°C under reduced pressure.

### Swelling Measurements

A series of aqueous solutions of NaCl, NaOH, and HCl were prepared. The dried and weighed hydrogel samples were immersed into each solution and allowed to swell to equilibrium, i.e., until constant weight was reached. The weight uptake of the gels was then determined as a difference, and the swelling degree was calculated using the following expression:

$$S_{wt} = W_e/W_o$$

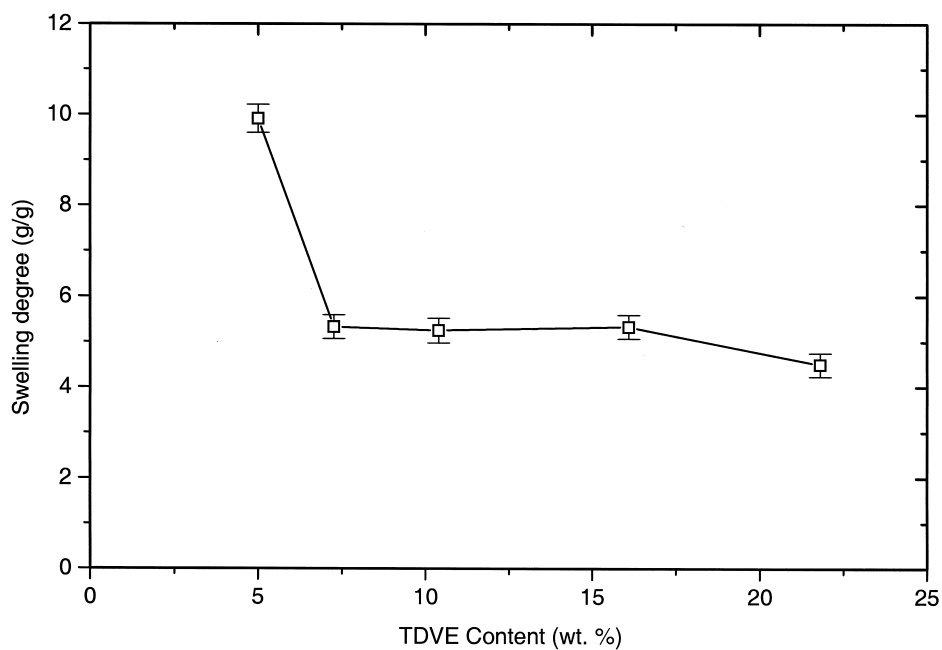
where  $W_e$  and  $W_o$  are the weight of the swollen hydrogel at equilibrium and the weight of the original dry sample, respectively. Each measurement was carried out three times, and then average values were calculated.

## RESULTS AND DISCUSSION

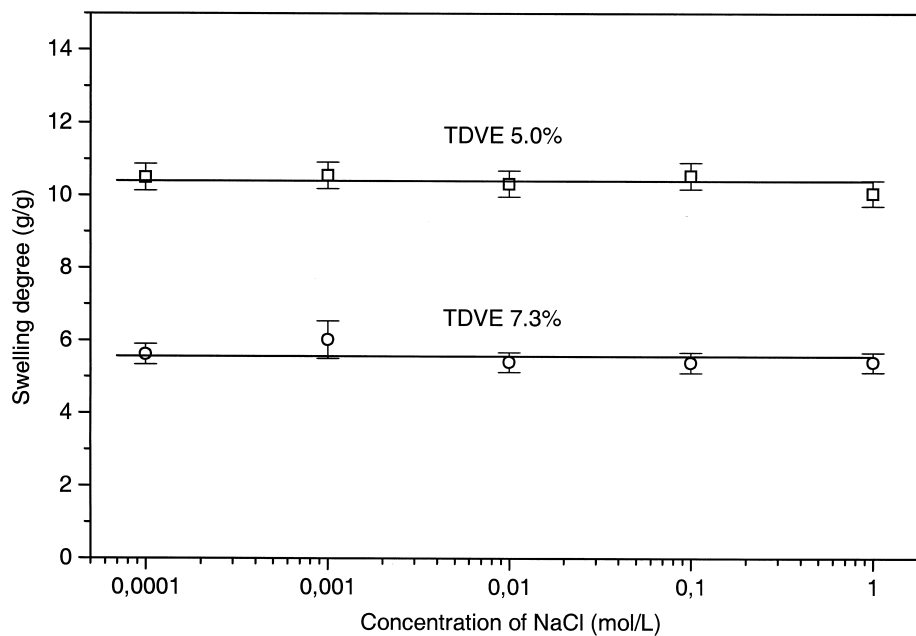
### Hydrogels Based on MTVE-TDVE Copolymers

Because of the high reactivity of boron trifluoride the reaction mixtures must be neutralized at low temperature, otherwise the copolymers could be deteriorated. It seems to be impossible to efficiently neutralize the initiator and remove it from the polymer bulk. Therefore, the precipitative polymerization that yields powdered products was chosen as a synthesis method. Methyl tert-butyl ether was found to be a suitable reaction medium, because it is a good solvent for the monomers, i.e., MTVE and TDVE, but does not dissolve poly(MTVE). The copolymerization carried out at low temperature ( $-78^{\circ}\text{C}$ ) yielded a fine suspension of the copolymer particles in methyl tert-butyl ether, and the initiator could then conveniently be neutralized by adding an equivalent amount of a methanolic ammonia solution. However, it was difficult to keep those particles as a powder at room temperature because of very low glass transition temperature of the copolymers produced. As a result, the particles quickly became sticky and agglomerated together at room temperature to form an apparently homogeneous polymer bulk.

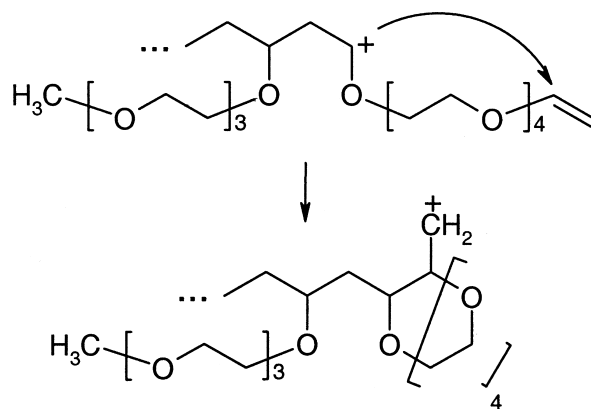
The dependence of the swelling degree of poly(MTVE) hydrogels on amount of TDVE used as a crosslinker is shown in Figure 1. As is seen from the Figure, the swelling degree of the hydrogels decreased with increasing content of the crosslinker, and the swellability was highest when the gels contained 5% of TDVE. When carried out at still lower concentrations of the crosslinker, the copolymerization only yielded soluble products, thus suggesting the formation of highly branched but not crosslinked polymers. Some side reactions of intramolec-



**Figure 1.** Swellability of poly(MTVE) gels in water vs. content of a crosslinker (TDVE).



**Figure 2.** Swellability of poly(MTVE-TDVE) gels in aqueous NaCl solutions versus concentration of NaCl.



*Scheme 1.*

ular cyclization of polymeric TDVE derivatives might also be involved in the overall process, as shown in Scheme 1.

In contrast, with an increasing content of TDVE above 7%, the swellability of the gels did not markedly change. Presumably, this can be accounted for by the length of the TDVE chain containing four ethylene oxide links, and by the same chemical nature of TDVE and MTVE, which implies the network flexibility remains nearly constant over a wide range of the TDVE content.

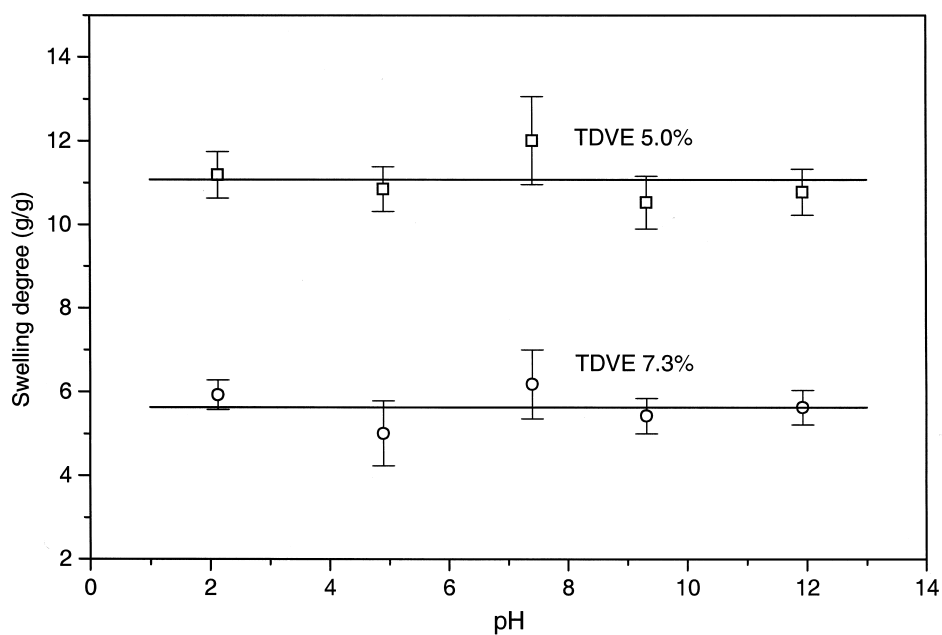
The dependence of the swelling degree of the gels in aqueous NaCl solutions as a function of the NaCl concentration is shown in Figure 2. It can be seen that the swellability of both gels did not depend on the presence of an electrolyte and remained the same over a wide range of concentrations from  $10^{-4}$  to 1 mol/L.

Figure 3 demonstrates stability of the swelling behavior of the poly(MTVE) gels under both basic and acidic conditions. As one could have expected, the swellability remained constant over a wide pH range from 2.0 to 12.0 at the fixed ionic strength of 0.02 mol/L.

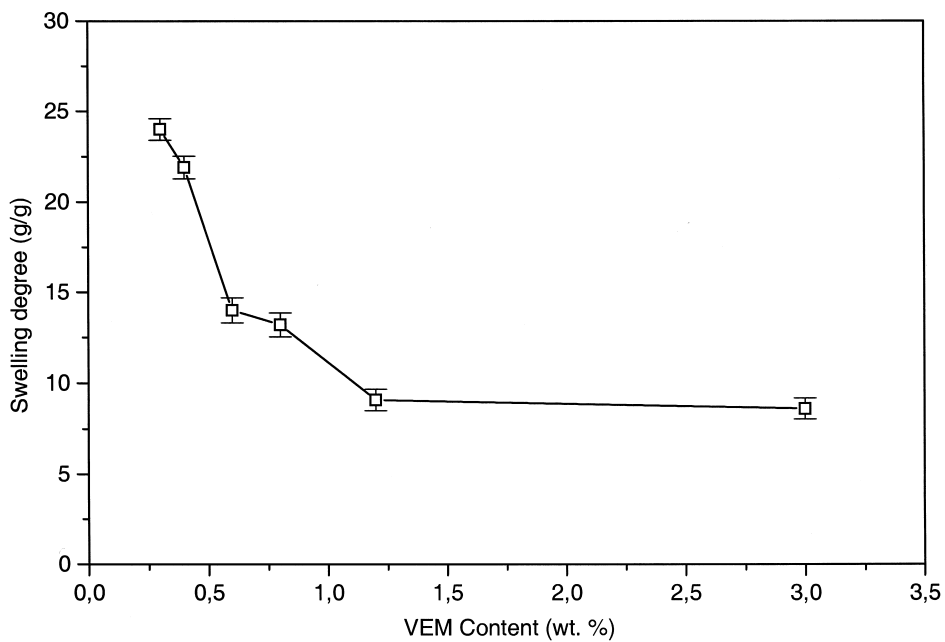
### Hydrogels Based on MTVE-VEM Copolymers

Using boron trifluoride etherate as an initiator, MTVE and VEM can readily be copolymerized in quantitative yields to afford soluble copolymers. The molecular weight distribution (MWD) of the copolymers (produced with 0.3 wt% of VEM and quantitative conversion) was found to be 4, as measured using a GPC technique (the relative number- and weight-average molecular weights were, respectively,  $M_n = 23,700$  and  $M_w = 96,700$ ). However, when synthesizing crosslinked networks, such a broad distribution does not much matter.

Copolymerizing MTVE with VEM at various monomer ratios, one can produce polymeric precursors containing variable amounts of crosslinkable methacrylate pendant groups. It was found that the copolymers lost their solubility in water, when they contained more than 5 wt% of VEM, due to its hydrophobic

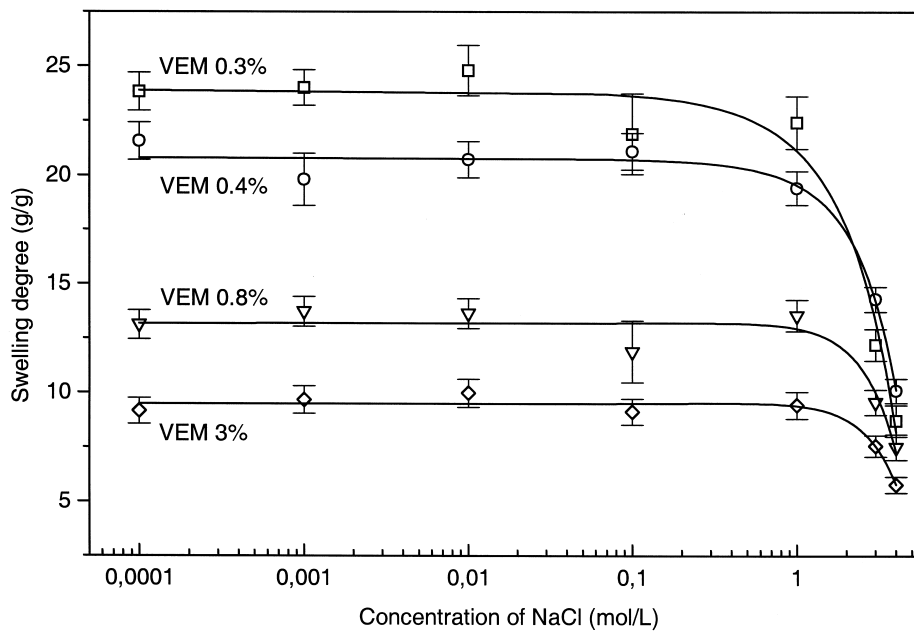


**Figure 3.** Swellability of poly(MTVE-TDVE) gels vs. pH of aqueous medium (ionic strength = 0.02 mol/L).

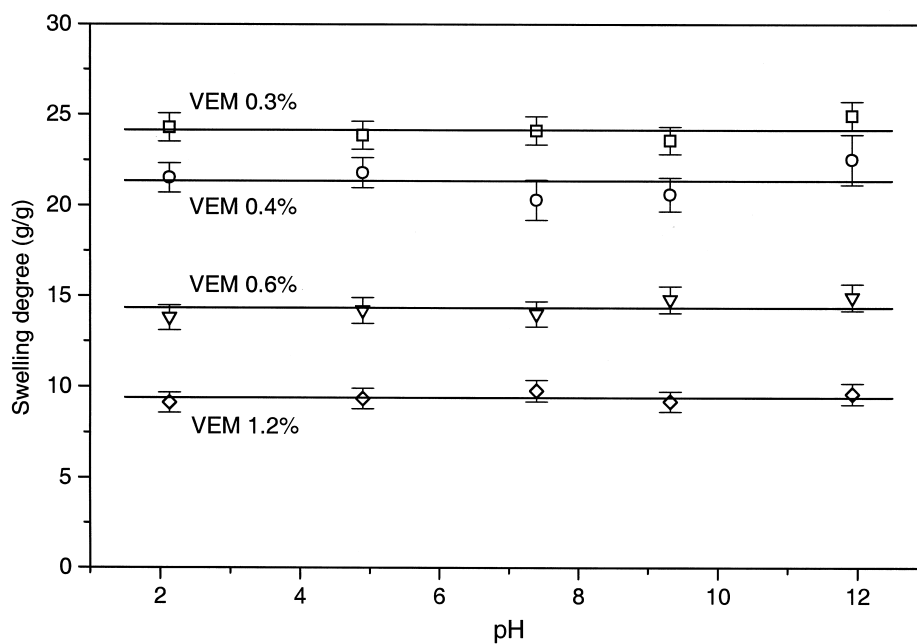


**Figure 4.** Swellability of poly(MTVE-VEM) gels in water vs. content of VEM.





**Figure 5.** Swellability of poly(MTVE-VEM) gels in aqueous NaCl solutions vs. concentration of NaCl.



**Figure 6.** Swellability of poly(MTVE-VEM) gels vs. pH of aqueous medium (ionic strength = 0.02 mol/L).

nature. Therefore, in order to synthesize hydrogels, the amount of the crosslinker should have been kept below 5 wt%.

Due to the presence of the methacrylate groups, the MTVE-VEM copolymers can be easily crosslinked with the use of conventional radical initiators, like an APS/TMED redox pair. It should be noted, however, that no crosslinking occurred, when the copolymers contained less than 0.3 wt% of VEM. The dependence of the swelling degree of poly(MTVE-VEM) hydrogels on amount of VEM is presented in Figure 4. Naturally, the highest swellability (24 g/g) was observed when the content of VEM was 0.3 wt% (crosslinkability threshold), i.e., when the network density was lowest.

Figure 5 demonstrates the effect of the electrolyte salt (NaCl) concentration upon swellability of the poly(MTVE-VEM) gels. One can see from the figure that the swelling degree did not change with increasing the salt concentration up to 1 mol/L. However, as the concentration of NaCl increased further, the swellability dropped. Presumably, such a behavior can be accounted for by the formation at higher NaCl concentrations of weak complexes between  $\text{Na}^+$  cations and oligoethylene oxide fragments, similarly to the complexes that form crown ethers with alkali metal cations. The formation of these complexes might increase the rigidity of an entire network, thereby causing its swellability to drop.

Figure 6 shows the dependence of the swelling degree of the poly(MTVE-VEM) hydrogels on pH of an aqueous medium. Similarly to poly(MTVE-TDVE), the swellability of the poly(MTVE-VEM) gels did not depend on pH over a wide range from 2 to 12.

## CONCLUSION

The two types of nonionic hydrogels were synthesized on the basis of MTVE by a cationic polymerization approach. The poly(MTVE-TDVE) gels were prepared by precipitative copolymerization of MTVE and TDVE directly using methyl tert-butyl ether as a polymerization medium. The gels containing 5 wt% of TDVE show their maximum swelling capacity to be 10 g/g.

The poly(MTVE-VEM) gels were produced by the two-step polymerization. Linear copolymers of MTVE and VEM were first synthesized by the low-temperature cationic copolymerization in dichloromethane. These copolymers were then crosslinked via a radical mechanism, using an APS/TMED redox pair as an initiator. The gels thus prepared reached their maximum swellability (24 g/g), when the content of VEM was 0.3 wt% (at the threshold of crosslinkability).

Being nonionic polymer networks, both types of the hydrogels generally demonstrated stable swelling behavior in the presence of an electrolyte salt as well as over a wide pH range of aqueous media.

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